

6.5.1 EQUIPMENT AND SUPPLIES

The equipment and supplies needed for making Eh measurements using the platinum electrode method are listed in table 6.5–1. Eh equipment must be tested before each field trip and cleaned soon after use. Every instrument system used for Eh measurement must have a log book in which all the equipment repairs and calibrations or equipment tests are recorded, along with the manufacturer make and model numbers and serial or property number.

Electrodes. Select either a redox-sensing combination electrode or an electrode pair (a platinum and reference electrode). **Use of the correct electrolyte filling solution is essential to proper measurement and is specified by the electrode manufacturer.** Orion Company, for example, recommends selection of a filling solution to best match the ionic strength of the sample solution, in order to minimize junction potentials.

Table 6.5–1. Equipment and supplies used for Eh measurements¹

[mV, millivolt; \pm , plus or minus; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least $\pm 1,400$ mV; BNC connector (see instrument specifications for pH meters, 6.4.1 in NFM 6.4)
- ✓ Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silver-chloride) or (b) combination electrode
- ✓ Electrode filling solutions (refer to manufacturer's specifications)
- ✓ Thermometer (liquid-in-glass or thermistor type), calibrated (see NFM 6.1 for selection and calibration criteria)—for use with millivolt meters without temperature compensator
- ✓ Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- ✓ Sampling system: (1) in situ (downhole) measurement instrument, or (2) submersible pump (used with closed-system flowthrough cell). Pump tubing must be "impermeable" to oxygen.
- ✓ ZoBell's solution
- ✓ Aqua regia or manufacturer's recommended electrode-cleaning solution
- ✓ Liquid nonphosphate laboratory-grade detergent
- ✓ Mild abrasive: crocus cloth or 400- to 600-grit wet/dry Carborundum™ paper
- ✓ Deionized water (maximum conductivity of $1.0 \mu\text{S}/\text{cm}$)
- ✓ Bottle, squeeze dispenser for deionized water
- ✓ Safety equipment: gloves, glasses, apron, chemical spill kit
- ✓ Paper tissues, disposable, lint free
- ✓ Waste-disposal container

¹Modify this list to meet specific needs of the field effort.

CAUTION: The standard hydrogen reference electrode (SHE) can be dangerous and is not recommended for field use.

- ▶ Silver:silver-chloride or calomel reference electrodes are the redox electrodes in common use.
- ▶ The Orion™ combination electrodes are platinum redox and silver:silver-chloride reference electrodes in one body (the Orion™ brand is used for purposes of illustration only).

ZoBell's solution. ZoBell's is the standard solution for testing redox instruments. ZoBell's solution can be obtained from the QWSU in Ocala, Fla., or it can be prepared fresh (see below). Quinhydrone solution is sometimes used but is not recommended because it is significantly less stable above 30°C and its temperature dependence is not as well defined as that of ZoBell's.

ZoBell's solution consists of a 0.1 molal KCl solution containing equimolal amounts of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. ZoBell's is reported stable for at least 90 days if kept chilled at 4°C. To prepare ZoBell's solution:

1. Weigh the chemicals (dry chemicals should be stored overnight in a desiccator before use).
 - 1.4080 g $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (Potassium ferrocyanide)
 - 1.0975 g $\text{K}_3\text{Fe}(\text{CN})_6$ (Potassium ferricyanide)
 - 7.4557 g KCl (Potassium chloride)
2. Dissolve these chemicals in deionized water and dilute solution to 1,000 mL.
3. Store the solution in a dark bottle, clearly labeled with its chemical contents, preparation date, and expiration date. Keep the solution chilled.

CAUTION: ZoBell's solution is toxic—handle with care.

Aqua regia. Aqua regia can be used for cleaning the Eh electrode (check the electrode manufacturer's recommendations). Prepare the aqua regia at the time of use—do not store it. To prepare the aqua regia, mix 1 volume concentrated nitric acid with 3 volumes of concentrated hydrochloric acid.

6.5.1.A MAINTENANCE, CLEANING, AND STORAGE

Refer to 6.4.1 of NFM 6.4 on pH for general guidelines on meter and electrode maintenance, cleaning, and storage. Follow the manufacturer's guidelines on the operation and maintenance of the meters and electrodes, and keep a copy of the instruction manual with each instrument system. Keep the meters and electrodes clean of dust and chemical spills, and handle them with care.

Maintenance

Keep the surface of noble electrodes clean of coatings or mineral deposits. A brightly polished metal surface prevents deterioration of electrode response. The billet tip is more easily cleaned than the wire tip on the platinum electrode. Condition and maintain the Eh electrodes as recommended by the manufacturer.

Cleaning

Keep the O-ring on electrodes moist during cleaning procedures.

- ▶ To remove precipitate that forms on the outside wall or tip of the reference or combination electrode, rinse the outside of the electrode with deionized water.
- ▶ If particulates or precipitates lodge in the space between the electrode sleeve and the inner cone of sleeve-type electrode junctions, clean the chamber by flushing out the filling solution (the precise procedure to be followed must come from the electrode manufacturer).
- ▶ To remove oily residues, use a liquid nonphosphate detergent solution and polish the surface with mild abrasive such as coarse cloth, a hard eraser, or 400- to 600-grit wet/dry Carborundum™ paper (Bricker, 1982).
- ▶ To recondition the Eh electrode, immerse the electrode in warm aqua regia (70°C) for about 1 minute. **Do not immerse the electrode for longer than 1 minute** because aqua regia dissolves the noble metal as well as foreign matter and leads to an erratic electrode response (Bricker, 1982). Soak the electrode several hours in tap water before use.

TECHNICAL NOTE: Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely needed. Additional cleaning and reconditioning procedures are discussed in NFM 6.4 and in American Public Health Association and others (1992), American Society for Testing and Materials (1990), Edmunds (1973), Adams (1969), and Callame (1968).

Storage

For short-term storage, immerse the electrode in deionized water to above the electrode junction and keep the fill hole plugged to reduce evaporation of the filling solution. The recommended procedures for long-term storage of electrodes vary with the type of electrode and by manufacturer. The Orion™ combination electrodes are stored dry after rinsing precipitates from outside of the electrode, draining the filling solution from the chamber, and flushing it with water (consult the manufacturer's cleaning instructions). The electrode connector ends must be kept clean. Clean them with alcohol, if necessary. Store the connector ends in a plastic bag when not in use.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.